CLEAN FUELS FROM COAL - AN ALTERNATIVE TO SNG

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INTRODUCTION

A major portion of current coal gasification research is directed toward processes for production of substitute natural gas (SNG). These processes rely typically on relatively low temperature, high pressure gasification to enhance methane yield in the gasifier, followed by extensive water gas shifting and acid gas removal, and finally a catalytic methanation step. Those portions of the SNG processes most critical to their success—high pressure gasification and methanation—are farthest from being proven technology.

The Methyl Fuel process, however, produces a clean liquid fuel, primarily methanol, from synthesis gas produced at medium pressures bypassing the problems of high pressure gasification. The process, shown schematically in Figure 1, is composed of operations each of which has been proven in commercial applications.

PROCESS DESCRIPTION

Synthesis begins with steam/oxygen gasification at 22 atm. or below and at temperatures well above 1500K (2240F). These conditions insure rapid reaction rates and high carbon utilization, with minimal problems in coal handling and feed. Steam gasification is accomplished in the upper chamber of a two-stage suspension gasifier, with heat being provided by combustion with oxygen of ungasified char recycled to the lower chamber. The resulting synthesis gas is virtually methane-free, consisting principally of hydrogen, steam and carbon oxides. Gasifiers of this type have been available commercially for many years. One example is the Belle, W. Va., gasifier built by B&W for duPont in the early 1950's.

Particulate removal is achieved by a cyclone system, which recycles the bulk of the unburned char back to the combustion zone of the gasifier, followed by a venturi-water scrub system which also cools the "make" gas.

Gaseous sulfur compounds are removed by a conventional hot carbonate scrubbing system, which also removes a portion of the CO_2 produced in the gasifier. Elemental sulfur is recovered as a salable byproduct in a conventional Claus plant. The sweetened synthesis gas is then reacted catalytically with steam in a water gas shift reactor to adjust the relative concentrations of hydrogen and carbon monoxide for Methyl Fuel synthesis. Shift requirements are about two-thirds of those needed for methanation.

A second hot carbonate scrubber removes most of the remaining CO_2, which is vented to the atmosphere. Hot carbonate systems were chosen here because of their well-known commercial acceptance and economy for removal of large quantities of acid gas, although other systems, such as the Rectisol system could also be used. In the latter case, methane absorption would be no problem in the Methyl Fuel process.

The sweet synthesis gas is then dewatered and compressed for alcohol synthesis, the degree of compression depending on the synthesis process used. In this study, we have chosen the Vulcan-Cincinnati, Inc. high pressure process partly because of the rugged nature and regenerability of its zinc-based catalyst.

Composition of the gas at this point is hydrogen and carbon monoxide in about a two-to-one ratio, with small amounts of CO_2, water, nitrogen, and methane. The carbon oxides react with hydrogen over a catalyst to form methanol and small amounts of higher alcohols and water. A condenser removes liquid products, which pass to a small refinery operation for purification. The finished product, trademarked Methyl Fuel, is a clean, sulfur and nitrogen-free liquid fuel suitable as a blending agent for gasoline and a substitute for light fuel oils. The fuel has a gross heating value just over 5500 kcal/kg (10,000 Btu/lb), and burns cleaner than natural gas.

A preliminary process study has shown that for suspension gasification without char recycle, where carbon losses are about 12 percent, we can expect an overall thermal efficiency of about 63.5 percent for the process. These figures are based on actual performance of the B&W Morgantown gasifier built for the Bureau of Mines in the early 1950's[1].

The above thermal efficiency seems low compared to efficiencies of 65-70 percent now being reported for competitive SNG processes, suggesting that some means may be available for improving process efficiency. Because of the nature of the high temperature gasification process, only a small number of products (CO, CO_2, H_2 and H_2O) are formed in significant quantities in the gasifier; and these are related through a mass balance and shift equilibrium. Thus a very simple expression can be derived to show the effects of certain gasification variables on Methyl Fuel production and thermal efficiency. Methyl alcohol is formed through the reactions:

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (1)$$
$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \qquad (2)$$

which are related through the water gas shift reaction,

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (3)$$

A simple molar balance based on these reactions shows that the maximum production of methyl alcohol is directly proportional to the moles of carbon monoxide and hydrogen formed in the gasifier, assuming that a shift converter is available to optimize the relative concentrations of CO and hydrogen, and that reactions (1) and (2) go to completion:

$$[CH_3OH] = 1/3\ ([CO] + [H_2]) \qquad (4)$$

If gasification is complete and methane and tar formation are negligible,

$$[CO] = [C]_f - [CO_2] \qquad (5)$$
$$[H_2] = [H_2]_f - [H_2O] \qquad (6)$$
$$[O_2]_f = [CO_2] + 1/2\ [CO] + 1/2\ [H_2O] \qquad (7)$$

where $[C]_f$, $[H_2]_f$ and $[O_2]_f$ are the moles of carbon, hydrogen and oxygen fed to the gasifier, excluding char recycle since it is already included in the coal feed, but including hydrogen and oxygen in the coal and steam feeds; and [CO], $[CO_2]$, $[H_2]$ and $[H_2O]$ are the moles of carbon oxides, hydrogen, and steam in the synthesis gas leaving the cyclone separators. Substituting and rearranging,

$$[CO] + [H_2] = 2([CO]_f - [O_2]_f) + [H_2]_f \tag{8}$$

From equation (4), then, recognizing that neither carbon gasification nor methyl alcohol formation may go to completion, and that side reactions occur

$$[CH_3OH] = n_M \frac{2(n_G [C]_f - [O_2]_f) + [H_2]_f}{3} \tag{9}$$

where $[CH_3OH]$ is the maximum number of moles of methyl alcohol produced, n_M and n_G represent the conversion efficiencies of methyl alcohol synthesis and gasification, respectively. Then n_G $[C]_f$ represents the number of moles of carbon leaving the gasifier as gaseous carbon oxides. For the purpose of this paper, we will assume complete conversion in the Methyl Fuel synthesis loop.

EFFECT OF CHAR RECYCLE

Using Equation (9), one can determine the effects of char recycle, CO_2 recycle, and steam addition on overall product yield and thermal efficiency. The B&W Morgantown gasifier may be used as a reference, producing 2.641 kmoles of Methyl Fuel for each 100 kg of West Virginia coal. Addition of char recycle raised the carbon utilization efficiency to 95 percent, the production of Methyl Fuel to 2.894 kmoles, and the overall thermal efficiency to 69.3 percent.

EFFECT OF CO_2 SUBSTITUTION

Substitution of CO_2 for oxygen represents one method for reducing oxygen costs. Off-gas from the hot carbonate scrubbers could be compressed and recycled back to the gasifier to take advantage of the Boudouard reaction:

$$C + CO_2 \longrightarrow 2CO \qquad (10)$$

Treating CO_2 as totally gasified carbon and oxygen, equation (9) shows that, with char recycle, a 10 percent molar substitution of CO_2 for oxygen increases the methanol yield to 3.048 moles/100 kg of coal, and the thermal efficiency of the synthesis process to 73.4 percent.

In actual practice, this efficiency would not be achieved since the Boudouard reaction places a heat penalty on the gasifier reducing the amount of process steam available for the remainder of the process. If this heat penalty is made up by combustion of coal in an auxiliary boiler, the overall process thermal efficiency is reduced to 70.6 percent as shown in Figure 2. Further substitution of CO_2 continues to improve the thermal efficiency of the process at the expense of gasification temperature until carbon utilization efficiency decreases, and methane and tars begin to form. At this point, equation (9) no longer holds, and gasification is not suitable for Methyl Fuel production.

EFFECT OF STEAM/OXYGEN RATIO

The effect of altering the steam/oxygen ratio may also be shown by equation (9). Steam substitution has the beneficial effect of increasing the hydrogen yield of the gasifier while decreasing the production of CO_2. Again using char recycle, a 10 percent molar substitution of steam for oxygen also increases the methanol yield to 3.048 moles/100 kg coal, and the apparent thermal efficiency to 73.4 percent. The steam gasification reaction

$$C + H_2O \longrightarrow CO + H_2 \qquad (11)$$

is also endothermic and places a heat penalty on the system. This reaction is less endothermic than the Boudouard reaction, however, resulting in a practical thermal efficiency of 70.8 percent.

The thermal penalties produced by CO_2 recycle and steam substitution are shown in Figure 3, expressed as percent of process heat available compared to that of the Morgantown gasifier. The thermal advantage of steam substitution is quite evident, especially at higher steam/oxygen ratios.

EFFECTS ON GAS TREATMENT

If it is assumed that the feed to the Methyl Fuel synthesis loop is balanced— i.e., in a two-to-one ratio of hydrogen to equivalent CO— then all excess carbon will leave the system as CO_2 via the carbonate scrubbers. Equation (9) and a simple carbon balance

$$[CO_2]_{scrubbed} = n_G [C]_f - [CH_3OH] \qquad (12)$$

will then show the effects of char recycle, CO_2 recycle and steam substitution on acid gas scrubbing load. Figure 4 illustrates these effects clearly, showing CO_2 absorber load as a percent of that required for the Morgantown gasifier case.

Raising carbon utilization efficiency to 95 percent by char recycle increases the ratio of CO to CO_2 in the gasifier and enhances the production of hydrogen. More usable carbon is produced, and the CO_2 absorber load drops to 91.7 percent of its original value. Since acid gas removal represents about 15 percent of the capital cost in a Methyl Fuel plant, and is one of the major users of process steam and electric power, the cost savings are significant.

CO_2 recycle has the effect of increasing the amount of CO_2 that must be absorbed. For every three moles of CO_2 recycled, one additional mole of CO_2 is absorbed. In a practical system, then, the cost of CO_2 compressors, added CO_2 absorber capacity, and additional process steam capacity would tend to offset any advantages due to an increase in overall process thermal efficiency.

Steam substitution has the reverse effect, reducing the amount of CO_2 discarded. For every three moles of steam substituted, two moles of CO_2 do not have to be absorbed. In addition to the capital cost savings, this route represents a more economical use of the process steam, since a typical hot carbonate stripper requires about three moles of steam for each mole of CO_2 absorbed. Operating with char recycle, a 10 percent steam substitution would reduce CO_2 absorber load by about 6 percent.

CONCLUSIONS

With few exceptions, today's SNG processes are years from commercialization or even demonstration. The Methyl-Fuel process, on the other hand, consists of components each of which has been demonstrated commercially, and thus could be readily commercialized. Overall process thermal efficiency is comparable to present SNG processes.

Because of the simplicity of the process and the gasification products produced, a simple expression relates gasifier feeds to Methyl Fuel output. This expression shows that char recycle, CO_2 recycle and steam substitution can all improve thermal efficiency, but all impose a heat penalty on the system. The combination of char recycle and steam substitution has been found most advantageous, since it maximizes thermal efficiency while minimizing the gasifier heat penalty and reducing capital costs and process steam requirements.

REFERENCES

1. P.R. Grossman and R.W. Curtis, "Pulverized-Coal-Fired Gasifier for Production of Carbon Monoxide and Hydrogen," Trans. ASME 76, pp. 689-95 (1954).

FIGURE 1

METHYL FUEL PROCESS FLOWSHEET

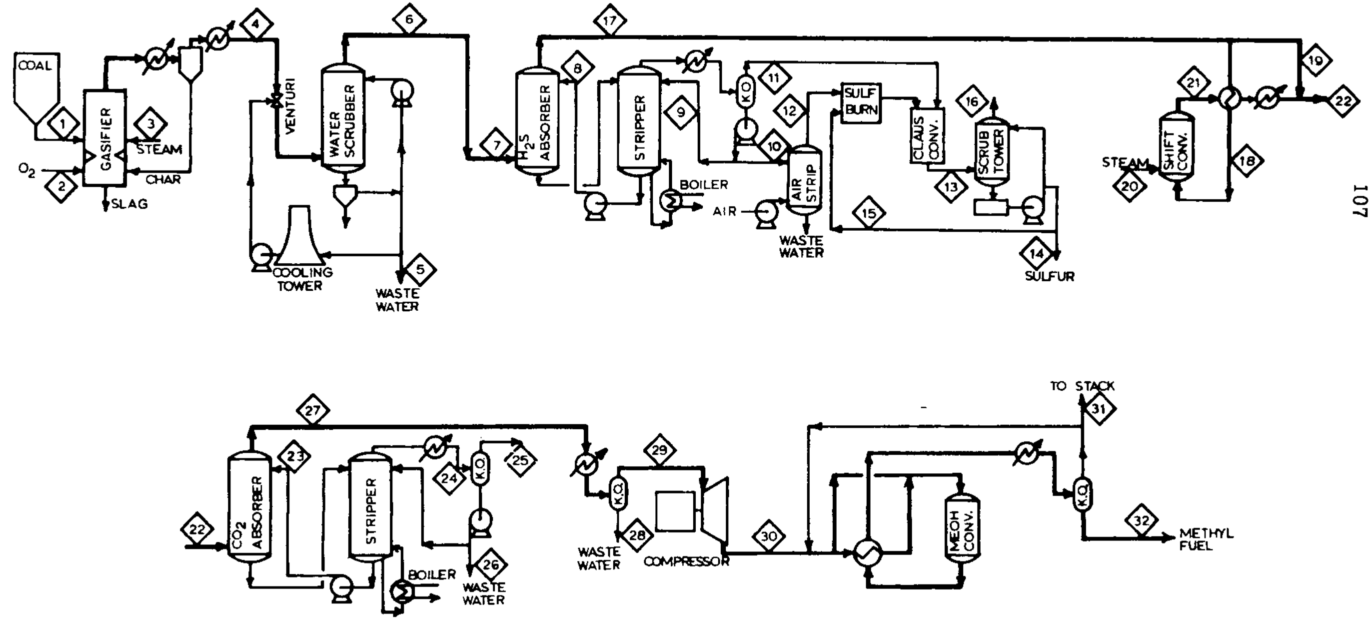

FIGURE 2

EFFECTS OF MODIFICATIONS IN GASIFIER OPERATION-THERMAL EFFICIENCY

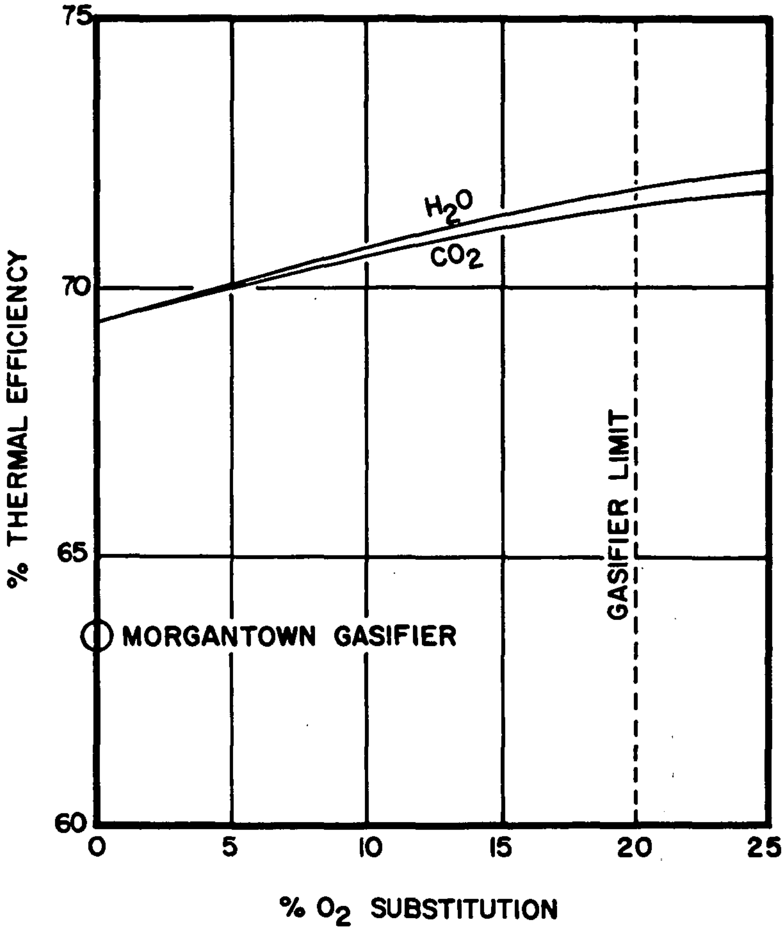

FIGURE 3

EFFECTS OF MODIFICATIONS IN GASIFIER OPERATION- ACID GAS REMOVAL

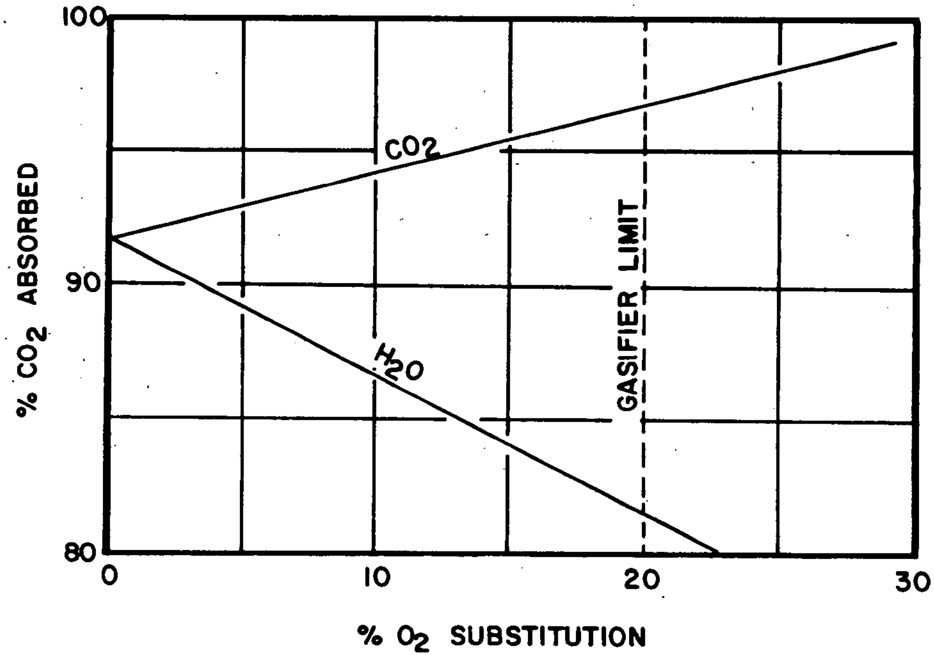

FIGURE 4

EFFECTS OF MODIFICATIONS IN GASIFIER OPERATION-STEAM GENERATION